Windecker, S. M. & Golding, N.

Deconvolve: a protocol and R package for thermogravimetric decay curve deconvolution for lignocellulosic biomass trait calculation

(what a mouthful….)

TG/DTG thermogravimetric/differential thermogravimetry

Get terminology straight about “pseudo compoenents”

Nomenclature table?

Could also just frame it as technique for package to do thermogravimetric analysis to determine lignocelluosic ompoasition of biomass—not in traits perspective… == more applicable. To biofuel etc?

Why do we need measures of lignocellulosic biomass?

Knowing composition of of biomass, namely hemi cell and lign contents important in a range of fields.

Plant litter characteristics are known to be important drivers of plant-soil interactions, particularly litter dynamics during decomposition. [REL TO OTHER ECO SERVICES?]. While litter of any type can become recalcitrant in the soil for a variety of reasons, including the absence of necessary decomposer communities or required environmental conditions, intrinsically chemically complex litter will almost always become recalcitrant. Litter quality, estimated by traits, is related to relative labillity or refractiveness of litter. It has been found to e a dominant driver of decay rate, stronger even than environmental variables (cor et al 2008), trait effects relate not just to leaf but also to root decay rates (freschet a plant eco spe), and across a range of ecosystems. Most of these studies include some method for calculation C fraction of components particularly lignin, which has been found to be a predominant predictor of litter decay (citations).

How do we currently measure?

Comvential chemical methods are .. environmental impact cost and time.

The most common method in the ecological literature to measure lignocellulosci biomass, consisting of hemicellulose and cellulose in addition to lignin, is wet chemistry aganlyses (makkonen, freschet – mult mech, freschet – plant econ). These techniques involve XXXXX (citations). Wet chemistry approaches are costly, and risky, and therefore not particularly wide-spread in the wider trait literature, despite its rel to decomposition, some papers did not measure at all (Quested, Albert – Helene, de Vries et al 2012). Calculation of lignocellulosic biomass is not even included in the trait handbook (perez), probably because current methods are more chemistry than traits. These items are measured in the decomp literature because of their known relationship, however lack of an easy measurement method probably restricting the number of studies examining their application in understanding response to changes (studies that look at trait responses to env) or to other eco functions, such as XXX, which may also be impacted by lignocellulosic biomass components. Other alternatives include liqueid chromatography (HPLC) and Nnear infraref spectroscopy (NIRS) -- (Birouste, and Rovira et al 2008) did NIRS, but TGA…

Alternative: TGA

Common in the biofuel field, lignocellulosic biomass components can be estimated using thermogravimetric analysis (Orfao & Figueiredo 2001, Barneto et al 2009, Cai & Liu 2007, Chen et al 2017). Independent … fix this info here. Using Barneto et al 2009

Labile peak a tlow or medium temperature and a recalcitrant oen at high temperatures. Lignin typically peaks the latest, but a strong peak may not be visible due to overlapping peaks, and because lignin is degraded over such a wide temperature range that the peak is very low (Duguy & Rovira 2010).

In this method a sample of biomass is pyrolised and mass over time is measured. In a constant temperature ramp over time this is equivalent to mass change over temperature. The derivative mass loss curve of each species is understood to correspond to the overall main components of biomass: hemicellulose, cellulose, and lignin. Changes in their relative abundance produce impact changes in the DTG curve. In order to estimate the mass loss of each pseudo-component, the overall DTG curve must be deconvolved into three requisite parts. Pseudo-components are a fraction of sample that does not necessarily correspond to a pure substance that thermally degrades in a specific way into a conctree temperature interval.

Pyrolysis described as sum of thermal degradation of main components: hc, cl, lg.

Pseudo-components were derived by deconvolving the mass loss rate curve into three curves. This will mean that the data assume all the mass lost within this temperature range is assigned to one of the three types.

In this study we used a three-part Frazer-Suzuki function mixture model to separate the curve into three components.

Barneto et al 2011 used tga to characterise the lignocellulosic composition of Eucalyptus wood. They foun comparable percent weight contributions as other studies that measured from scratch (Brito et al 2008). Also Orfao et al 1999

Different math models

Cheng et al 2015 (applicability of fs…), Hu et al 2016 (thermo kinetics…) used Fraser-Suzuki.

Sun et al 2015 (kinetic study…) used asymmetric bi-Gaussian

Chen et al 2017 (thermo pyrolysis… ) used asymmetric double sigmoidal

Perejon et al 2011 (kinetic analysis…) compared Gaussian, Lorentzian, Weibull, and Fraser-Suzuki. Found that Lorentzian and Gaussian are not appropriate because inetic curves are asymmetrical. Showne that fs fits any kinetic curve. Is able to fit curves that follow ideal models as well as those that deviate due to inhomogeneity. Recommend using fs for peak deconvolution of complex reaction into individual processes, and then subsequent kinetic analysis.

The fuels researchers use this technique to estimate kinestic parameters of materials. In practice, those who use TGA often report using a peak fitting software. This is neither reproducible nor transparent, often does not even specify which mathematical form was used. This R package seeks to fill this gap to both increase the reproducibility of this work, as well as to make this method of lignocell approx. more available to traits researchers. Easy, inexpensive, standardised.

A protocol for lignocellulosic biomass calculation using deconvolve

As described more fully in (Windecker et al 2017).

As with leaf traits in Perez, should collect 10 leaf samples of robust, well-grown individuals.

Litter should be pooled and dried and ground to ~ size.

TG analysis

~10-20 mg of sample should be place in the crucible.

N2 atmosphere over a temperature ramp of 30-800 C at 10C/min.

Raw mass loss data imported into the statistical software R.

Deconvolve package

Mass loss rate was calculated by taking the derivative.

After integrating the curves, you have the mixing proportions of each. These can then be modified by the amount of carbon left in the ash sample to calculate mg component per mg dry weight.

Function inputs: lower, upper

* Data were clipped at 120C and at 600C. 120 C effectively standardises to dry weight, as mass loss before that temperature is considered dehydration water loss. Lignocellulosic components are not considered to be lost about about 600. Mass lost after that is typically interacting with volatiles.

Sample Results – this has been implemented in (Windecker et al. xxxx)

Illustrate with a few different materials. Seagrass sample, woody, gramin, forb? Pure cellulose

Discussion

Limitations

* developed using wetland plants
* some of the initial values will not be appropriate for litter that is too different or that needs to be deconvolved into too many other ocmpoennts. Ex. Woody.

Conclusion

Lignocellulosic biomass calculation with TGA is already relatively inexpensive, this package enables its application to be more widespread by improving ease of use and standardising methods for calculation. using this method is a good candidate for more widespread application in the trait literature. In combination with this package, it is now much more accessible to the majority of ecologists. It is also makes this method more transparent and reproducible.

In this study, I examine a novel method in ecology for calculating lignocellulosic biomass using mixture modelling of thermogravimetric analysis (TGA), typical in the biofuel field. I found that TGA coupled with modelling approaches is a rapid, low-cost assessment method that can be used to estimate partitioning of leaf carbon.

Acknowledgements: Stacey Trevathan-Trackett, Peter Vesk, Jack